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**Japanese Patent Application No. 2001-012493**

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## SPECIFICATION

### Title of the Invention

MEMBRANE ELECTRODE ASSEMBLY AND METHOD FOR PRODUCING  
5 SAME, AND POLYMER ELECTROLYTE FUEL CELL COMPRISING SUCH  
MEMBRANE ELECTRODE ASSEMBLIES

### Claims:

1. A membrane electrode assembly comprising a polymer electrolyte  
10 membrane, said polymer electrolyte membrane having a softening point of  
120°C or more and a Q value of 0.09-0.18 C/cm<sup>2</sup>.
2. The membrane electrode assembly according to claim 1 wherein  
said polymer electrolyte membrane is made of a sulfonated, non-fluorinated  
polymer that may contain oxygen in its skeleton or other substituent groups  
15 than a sulfonic group.
3. The membrane electrode assembly according to claim 2, wherein  
said sulfonated, non-fluorinated polymer is selected from the group consisting  
of sulfonated polyetheretherketone, sulfonated polysulfone, sulfonated  
polyethersulfone, sulfonated polyetherimide, sulfonated polyphenylene  
20 sulfide and sulfonated polyphenylene oxide.
4. A method for producing a membrane electrode assembly comprising  
a polymer electrolyte membrane according to any one of claims 1 to 3, said  
method comprising the steps of:  
forming said polymer electrolyte membrane from a solution of said  
25 polymer electrolyte;  
hot-pressing said polymer electrolyte membrane and a pair of electrodes  
arranged on both sides of said membrane, while the amount of said organic  
solvent remaining in said polymer electrolyte membrane is 3-20 weight %;  
and then

drying said polymer electrolyte membrane.

5. The method for producing a membrane electrode assembly according to claim 4, wherein said organic solvent is N-methylpyrrolidone.

6. A polymer electrolyte fuel cell comprising stacking a plurality of the

5 above membrane electrode assemblies according to any one of claims 1 to 3.

## DETAILED EXPLANATION OF THE INVENTION

[0001]

### Field of the Invention

The present invention relates to a membrane electrode assembly comprising a polymer electrolyte membrane and a method for producing such a membrane electrode assembly and a polymer electrolyte fuel cell comprising it, particularly, to a membrane electrode assembly comprising a polymer electrolyte membrane having improved heat resistance without suffering from deterioration of power-generating performance and a polymer electrolyte fuel cell comprising it.

[0002]

### Prior Art

As the depletion of oil resources, global warming, etc. have been becoming serious environmental problems, much attention has been paid to fuel cells as clean power sources for motors, and wide development is now carried out to put them in part into practical use. Particularly when fuel cells are mounted in automobiles, etc., they are preferably polymer electrolyte fuel cells comprising polymer electrolyte membranes, whereby widely used as the polymer electrolyte membranes are ion exchange membranes of sulfonated, fluorinated resins such as Nafion<sup>®</sup> (available from du Pont) and Flemion<sup>®</sup> (available from Asahi Glass Co., Ltd.).

[0003]

A membrane electrode assembly for a polymer electrolyte fuel cell comprising a polymer electrolyte membrane is produced by hot-pressing the polymer electrolyte membrane and electrodes at higher temperatures than the softening point of the polymer electrolyte membrane. Because there is a large contact area between a catalytic layer of each electrode and the polymer electrolyte membrane in the membrane electrode assembly produced by

hot-pressing, a fuel cell comprising such membrane electrode assembly is advantageous in having a high power-generating performance.

[0004]

However, because there is increasing demand to provide fuel cells with higher power, a polymer electrolyte membrane having such a high heat resistance as to make it possible to endure high-temperature operation has become needed. Because the polymer electrolyte membrane having a high heat resistance has a high softening point, it should be hot-pressed at higher temperatures than for the conventional membranes. In this case, however, part of a polymer structure of the polymer electrolyte is thermally decomposed, resulting in the deterioration of power-generating performance of the fuel cells.

[0005]

#### **Problems to be Solved by the Invention**

Accordingly, an object of the present invention is to provide a membrane electrode assembly comprising a polymer electrolyte membrane having not only a high power-generating performance but also such a high heat resistance that it is not decomposed by high-temperature hot-pressing.

[0006]

Another object of the present invention is to provide effectively a method for producing such a membrane electrode assembly.

[0007]

Still another object of the present invention is to provide a polymer electrolyte fuel cell comprising stacking a plurality of the above membrane electrode assemblies.

[0008]

#### **Means for Solving the Problems**

Thus, the membrane electrode assembly of the present invention

comprises a polymer electrolyte membrane having a softening point of 120°C or more and a Q value of 0.09-0.18 C/cm<sup>2</sup>.

[0009]

The polymer electrolyte membrane having the above properties is preferably made of a sulfonated, non-fluorinated polymer. The sulfonated, non-fluorinated polymer is particularly preferably selected from the group consisting of sulfonated polyetheretherketone, sulfonated polysulfone, sulfonated polyethersulfone, sulfonated polyetherimide, sulfonated polyphenylene sulfide and sulfonated polyphenylene oxide.

[0010]

A method of the present invention for producing the membrane electrode assembly above comprises the steps of: forming the polymer electrolyte membrane from a solution of the polymer electrolyte; hot-pressing the polymer electrolyte membrane and a pair of electrodes arranged on both sides of the membrane, while the amount of the organic solvent remaining in the polymer electrolyte membrane is 3-20 weight %; and then drying the polymer electrolyte membrane. As the organic solvent above, N-methylpyrrolidone is preferably used.

[0011]

The polymer electrolyte fuel cell of the present invention is constituted by stacking a plurality of the above membrane electrode assemblies via separator plates.

[0012]

#### **Mode for Carrying Out the Invention**

##### **[1] Membrane electrode assembly**

The membrane electrode assembly of the present invention comprises a polymer electrolyte membrane and a pair of electrodes on both sides thereof.



[0013]

(A) Polymer electrolyte membrane

The polymer electrolyte membrane of the present invention comprises preferably sulfonated, non-fluorinated polymers. The sulfonated, non-fluorinated polymers include non-fluorinated polymers having a carbonyl (-CO-) group, an ether (-O-) group, a sulfone (-SO<sub>2</sub>-) group, a sulfide (-S-) group, an imide (-NH-) group, etc. in polymer skeletons or substituent groups composed of hydrocarbons. Specific examples of these sulfonated, non-fluorinated polymers are particularly sulfonated polyetheretherketone, sulfonated polysulfone, sulfonated polyethersulfone, sulfonated polyetherimide, sulfonated polyphenylene sulfide and sulfonated polyphenylene oxide. These sulfonated, non-fluorinated polymer preferably has an ion exchange capacity (milli-equivalent of the sulfonic group per 1 g) of 1-2.6 meq/g. If its ion exchange capacity were less than 1 meq/g, it would fail to exhibit sufficient power-generating performance when formed into a polymer electrolyte membrane. On the other hand, if its ion exchange capacity were more than 2.6 meq/g, it would have insufficient heat resistance when formed into a polymer electrolyte membrane.

[0014]

The sulfonated, non-fluorinated polymer has a softening point (temperature at which their kinetic viscosity decreases) of 120°C or higher. When the softening point is lower than 120°C, the polymer electrolyte membrane has insufficient heat resistance, likely to be thermally decomposed during hot pressing. The preferred softening point of the sulfonated, non-fluorinated polymer is 125-300°C.

[0015]

The polymer electrolyte membrane comprising the sulfonated, non-fluorinated polymers preferably has a thickness of about 20-60 μm.

When the thickness is less than about 20  $\mu\text{m}$ , the electrodes are likely to be short-circuited. On the other hand, when the thickness is more than about 60  $\mu\text{m}$ , a sufficient power-generating performance cannot be obtained.

[0016]

5           The polymer electrolyte membrane should have a Q value (charge per a unit area) of 0.09-0.18  $\text{C}/\text{cm}^2$ . When the Q value is less than 0.09  $\text{C}/\text{cm}^2$ , it is impossible to obtain sufficient power-generating performance. On the other hand, when it exceeds 0.18  $\text{C}/\text{cm}^2$ , the polymer electrolyte membrane has too low heat resistance, resulting in too high percent defective.

10   The particularly preferable Q value of the polymer electrolyte membrane is 0.14-0.18  $\text{C}/\text{cm}^2$ . Here, the Q value is the amount of electric charge per a unit area determined from a peak area of proton on an adsorption side in the scanning of voltage from -0.1 V to +0.7 V, in a cell in which the amount of platinum in the catalytic layer of each electrode is 0.5  $\text{mg}/\text{cm}^2$ , and in which a

15   polymer electrolyte membrane electrode assembly is surrounded by an aqueous sulfuric acid solution of pH 1 on one side and a nitrogen gas on the other side. The Q value may be regarded as an indicator of adhesion of the electrode to the polymer electrolyte membrane, and it has been found that with the Q value of 0.09-0.18  $\text{C}/\text{cm}^2$ , an excellent polymer electrolyte

20   membrane-electrode assembly is obtained.

[0017]

          The measurement method of the Q value will be explained in detail referring to Fig. 1. A polymer electrolyte membrane-electrode assembly to be measured comprises a polymer electrolyte membrane 1 and an electrode 10

25   formed on only one surface of the membrane 1. The electrode 10 is composed of a catalytic layer 2 and a diffusion layer 3 (primary layer 4 and carbon paper 5). The polymer electrolyte membrane 1 is in contact with an aqueous sulfuric acid solution 9 of pH 1 on a side free from the electrode 10

and with a nitrogen gas on the side of the electrode 10. A reference electrode 8 is immersed in an aqueous sulfuric acid solution 9, while a control electrode 7 immersed in the aqueous sulfuric acid solution 9 is connected to the diffusion layer 3 of the membrane electrode assembly.

5 [0018]

When voltage is applied between the diffusion layer 3 and the aqueous sulfuric acid solution 9 by a potentiostat 6, protons in the aqueous sulfuric acid solution 9 pass through the polymer electrolyte membrane 1 to the electrode 10, whereby electrons are exchanged. That is, as protons are  
10 attracted to the platinum surface in the catalyst particles, electrons are given from platinum. In an opposite case, electrons are transferred from the adsorbed hydrogen atoms to platinum and diffused as protons into the aqueous sulfuric acid solution.

[0019]

15 By scanning voltage from -0.1 V to +0.7 V, the Q value ( $C/cm^2$ ) can be determined from the proton peak area on the adsorption side. A typical measurement example is shown in Fig. 2. In the discharge curve shown in Fig. 2, the Q value is defined as the amount of electric charge per a unit area of the membrane electrode assembly, indicating that the larger the Q value,  
20 the higher the adhesion of the electrode 10 to the polymer electrolyte membrane 1.

[0020]

(B) Electrode

The electrodes (oxygen electrode and fuel electrode) laminated on  
25 both sides of the polymer electrolyte membrane each consist of a diffusion layer and a catalytic layer.

[0021]

(1) Diffusion layer

The diffusion layer preferably comprises a carbon paper and a primary layer formed thereon. The primary layer contains conductive particles (carbon black particles) and water-repellant particles [polytetrafluoroethylene (PTFE) particles] in a weight ratio of carbon black particles to PTFE of 1/3-5/1. When the weight ratio of carbon black particles to PTFE particles is less than 1/3, the diffusion layer has insufficient electric conductivity. Also, it is not useful to make the weight ratio more than 5/1.

[0022]

10 (2) Catalytic layer

The catalytic layer formed on the electrode diffusion layer comprises uniformly dispersing catalyst particles of platinum particles carried on carbon black particles in an ion-conducting binder. The ion-conducting binders may be the above sulfonated, non-fluorinated polymers as well as other ion exchange resins such as Nafion<sup>®</sup>, etc. A weight ratio of the platinum particles to the carbon black particles is preferably 1/4-2/1, and a weight ratio of the catalyst particles (platinum particles + carbon black particles) to the ion-conducting binder is preferably 1/2-3/1.

[0023]

20 [2] Method for producing membrane electrode assembly

(A) Formation of polymer electrolyte membrane

A solution of a sulfonated, non-fluorinated polymer in an organic solvent is formed into a membrane having a thickness corresponding to a dry thickness of 20-60  $\mu\text{m}$  by a solution-casting method, etc. The preferred organic solvents are N-methylpyrrolidone, dimethyl sulfoxide, dimethyl acetamide, etc.

[0024]

Although a drying treatment is carried out after forming the

membrane, it does not completely dry the membrane, but the amount of organic solvent remaining in the membrane is preferably adjusted to 3-20 weight %. Because the sulfonated, non-fluorinated polymer has a high softening point, the workability of the membrane should be improved by causing a small amount of an organic solvent to remain in the membrane. Accordingly, when the amount of the remaining organic solvent is less than 3 weight %, hot-pressing needs high temperature to closely adhere the polymer electrolyte membrane to the electrode, resulting in likelihood of the decomposition of the sulfonic group, etc. in the polymer electrolyte membrane. On the other hand, when the amount of the remaining organic solvent exceeds 20 weight %, the polymer electrolyte membrane is so soft that it is likely to be ruptured during hot-pressing, and that it takes too much time to remove an organic solvent after the hot-pressing. The more preferred amount of the remaining organic solvent is 5-15 weight %.

[0025]

#### (B) Formation of electrode

##### (1) Production of diffusion layer

A slurry comprising carbon black particles and particles of polytetrafluoroethylene (PTFE) uniformly dispersed in ethylene glycol is coated on a carbon paper, and followed by drying.

[0026]

##### (2) Production of catalyst slurry

Carbon black particles are caused to carry platinum particles to form catalyst particles. The resultant catalyst particles are uniformly dispersed in a solution of an ion-conducting binder (solvent: N-methylpyrrolidone, etc.) to produce a catalyst paste. The catalyst paste thus obtained is screen-printed on a surface of the diffusion layer on each carbon paper, and followed by drying to form a catalytic layer.

[0027]

(3) Production of membrane electrode assembly

The polymer electrolyte membrane in which 3-20 weight % of an organic solvent remains is sandwiched by an oxygen electrode and a fuel electrode each constituted by the above electrode is hot-pressed to produce a membrane electrode assembly. The hot-pressing conditions are in general preferably a temperature of 60-200°C and a pressure of 1-10 MPa for 1-5 minutes. Although a sulfonated, non-fluorinated polymer has a softening point of 120°C or above, the hot-pressing temperature may be at least about 120°C, because the membrane contains a small amount of an organic solvent. With respect to the upper limit of the hot-pressing temperature, it is preferably 160°C or below to prevent the polymer structure of the polymer electrolyte membrane from suffering thermal decomposition.

[0028]

Although hot-pressing may be carried out only once, it may consist of a first hot-pressing at relatively low temperature, and then a second hot-pressing at a relatively high temperature for a short period of time. In this case, the first hot pressing conditions are about 60-100°C (for instance, about 80°C) and about 1-10 MPa (for instance, about 2.5 MPa) for about 1-5 minutes (for instance, 2 minutes), and the second hot pressing conditions are about 120-200°C (for instance, 160°C) and about 1-10 MPa (for instance, about 3 MPa) for about 1-5 minutes (for instance, 1 minute).

[0029]

After carrying out the hot pressing, the polymer electrolyte membrane sandwiched by a pair of is dried to remove completely the remaining organic solvent.

[0030]

**EXAMPLES**

The present invention will be described in detail referring to  
EXAMPLES below without intention of limiting the present invention thereto.

[0031]

EXAMPLE 1

5 (1) Production of polymer electrolyte membrane

Polyetheretherketone (PEEK) was introduced into fuming sulfuric acid so that it was sulfonated to an ion exchange capacity (milli-equivalent of a sulfonic group per 1 g) of 1.25 meq/g, thereby obtaining sulfonated polyetheretherketone. The resultant sulfonated polyetheretherketone was  
10 dissolved in N-methylpyrrolidone as an organic solvent while refluxing, to form a sulfonated polyetheretherketone solution at a concentration of 12 weight %. Using this sulfonated polyetheretherketone solution, there was produced a polymer electrolyte membrane having a thickness of 50  $\mu\text{m}$  (solvent content: 5 weight %) by a solution-casting method.

15 [0032]

(2) Production of catalyst paste

Carbon black particles (furnace black) were subjected to carrying platinum particles at a weight ratio of 1:1 to produce catalyst particles. In addition, using a Nafion<sup>®</sup> resin (available from du Pont) as an ion-conducting  
20 binder, the catalyst particles were uniformly dispersed in a Nafion<sup>®</sup> resin solution to produce a catalyst paste at a weight ratio (catalyst particles: Nafion<sup>®</sup> resin) of 8:5.

[0033]

(3) Production of diffusion layer

25 A slurry obtained by dispersing carbon black particles (furnace black) and polytetrafluoroethylene (PTFE) particles in ethylene glycol was coated on one surface of a carbon paper, which was dried to provide a diffusion layer.

[0034]

(4) Production of electrode

A catalyst paste obtained in the step (2) was screen-printed on a primary layer of the diffusion layer, and after drying at 60°C for 10 minutes, vacuum drying was carried out at 120°C for 60 minutes to form a catalytic layer on the diffusion layer. Incidentally, the concentration of the catalyst paste coated was adjusted such that the amount of platinum on the electrode was 0.5 mg/cm<sup>2</sup>. Thus, a pair of an oxygen electrode and a fuel electrode was obtained.

[0035]

(5) Production of membrane electrode assembly

The polymer electrolyte membrane obtained in the above step (1), which contained 5 weight % of an N-methylpyrrolidone organic solvent, was sandwiched by the oxygen electrode and the fuel electrode obtained in the above step (4), and hot-pressed at a temperature of 120°C and a pressure of 2.5 MPa for 2 minutes to produce a membrane electrode assembly. The resultant membrane electrode assembly was introduced into a vacuum furnace to completely dry the polymer electrolyte membrane.

[0036]

EXAMPLE 2

A membrane electrode assembly was produced in the same manner as in EXAMPLE 1, except that using a polymer electrolyte membrane containing 3 weight % of an N-methylpyrrolidone organic solvent in the step (5) of EXAMPLE 1, hot-pressing was carried out at a temperature of 150°C and a pressure of 2.5 MPa for 2 minutes.

[0037]

EXAMPLE 3

A membrane electrode assembly was produced in the same manner



as in EXAMPLE 1, except for carrying out a first hot-pressing at a temperature 80°C and a pressure of 2.5 MPa for 2 minutes in the step (5) of EXAMPLE 1, and then carrying out a second hot-pressing at a temperature 160°C and a pressure of 3 MPa for 1 minute.

5 [0038]

EXAMPLE 4

A membrane electrode assembly was produced in the same manner as in EXAMPLE 1, except that using a polymer electrolyte membrane containing 10 weight % of an N-methylpyrrolidone organic solvent in the step  
10 (5) of EXAMPLE 1, hot-pressing was carried out at a temperature of 160°C and a pressure of 2.5 MPa for 2 minutes.

[0039]

COMPARATIVE EXAMPLE 1

A membrane electrode assembly was produced in the same manner  
15 as in EXAMPLE 1, except that using a polymer electrolyte membrane containing 1 weight % of an N-methylpyrrolidone organic solvent, hot-pressing was carried out at a temperature of 120°C and a pressure of 2.5 MPa for 2 minutes in the step (5) of EXAMPLE 1.

[0040]

20 COMPARATIVE EXAMPLE 2

A membrane electrode assembly was produced in the same manner as in EXAMPLE 1, except that using a polymer electrolyte membrane containing 25 weight % of an N-methylpyrrolidone organic solvent, hot-pressing was carried out at a temperature of 180°C and a pressure of 2.5  
25 MPa for 2 minutes in the step (5) of EXAMPLE 1.

[0041]

Evaluation of EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1 and 2

(1) Measurement of Q value

Using an apparatus shown in Fig. 1, the Q value of each membrane electrode assembly in EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1 and 2 was measured in a range from -0.1 V to +0.7 V. The measurement results are shown in Table 1.

[0042]

(2) Measurement of generated voltage

Using a single cell comprising each membrane electrode assembly in EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1 and 2, electric power was generated with the air supplied to an oxygen electrode and pure hydrogen supplied to a fuel electrode, and cell voltage V was measured at a current density  $i$  of 0.2 A/cm<sup>2</sup>. The measurement conditions were pressure of 100 kPa, utility percentage of 50%, relative humidity of 50% and a temperature of 85°C for both of the oxygen electrode and the fuel electrode. The measurement results are shown in Table 1 and Fig. 3(a).

[0043]

(3) Measurement of percent defective

Using a single cell comprising each membrane electrode assembly of EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1 and 2, a He gas at a pressure of 0.5 kPa was supplied to the cell from one side to measure the volume of a He gas passing through the cell to the other side per a unit time, thereby determining the amount of He leaked. By measuring 50 cells for each EXAMPLE and COMPARATIVE EXAMPLE, those in which the amount of He leaked was 0.1 ml/(cm<sup>2</sup> x minute) or more were counted as defective products. The results are shown in Table 1 and Fig. 3(a).

[0044]

Table 1

Membrane electrode assembly comprising polymer electrolyte membrane  
made of sulfonated polyetheretherketone

No.	Q value (C/cm <sup>2</sup> )	Remaining Solvent (wt. %)	Hot-pressing		Percent Defective	Generated Voltage
			First	Second		
COM. EX. 1	0.05	1	120°C, 2.5 MPa, 2 min.	--	< 1%	0.62 V
EXAMPLE 1	0.09	5	120°C, 2.5 MPa, 2 min.	--	< 1%	0.71 V
EXAMPLE 2	0.12	3	150°C, 2.5 MPa, 2 min.	--	< 1%	0.79 V
EXAMPLE 3	0.14	5	80°C, 2.5 MPa, 2 min.	160°C, 3 MPa, 1 min.	< 1%	0.81 V
EXAMPLE 4	0.18	10	160°C, 2.5 MPa, 2 min.	--	< 1%	0.80 V
COM. EX. 2	0.20	25	180°C, 2.5 MPa, 2 min.	--	11%	0.82 V

5

[0045]

As is clear from Table 1 and Fig. 3(a), when the Q value of the membrane electrode assembly is less than 0.09 C/cm<sup>2</sup>, only low voltage is generated. On the other hand, when the Q value is more than 0.18 C/cm<sup>2</sup>,

10 there is high percent defective. Accordingly, in the membrane electrode assembly having sulfonated polyetheretherketone used as a sulfonated, non-fluorinated polymer, the polymer electrolyte membrane should have a Q value of 0.09-0.18 C/cm<sup>2</sup>.

[0046]

15 EXAMPLE 5

(1) Production of polymer electrolyte membrane

Polysulfone was introduced into fuming sulfuric acid to form sulfonated polysulfone having an ion exchange capacity of 1.5 meq/g. It was dissolved in N-methylpyrrolidone as an organic solvent while refluxing to obtain a sulfonated polysulfone solution having a concentration of 10 weight %. Using this solution, there was produced a polymer electrolyte membrane having a thickness of 40  $\mu\text{m}$  (solvent content: 5 weight %) by a solution-casting method.

[0047]

#### (2) Production of catalytic layer

Carbon black particles (furnace black) were subjected to carrying platinum particles having an average particle size of 350 nm at a weight ratio of 1:1 to produce catalyst particles. Also, using a Nafion<sup>®</sup> resin (available from du Pont) as an ion-conducting binder, the catalyst particles were uniformly dispersed in a solution of the Nafion<sup>®</sup> resin in N-methylpyrrolidone as a solvent, to produce a catalyst paste in which a weight ratio of the catalyst particles to the Nafion<sup>®</sup> resin was 1:1.

[0048]

#### (3) Production of diffusion layer

A slurry obtained by dispersing carbon black particles (furnace black) and polytetrafluoroethylene (PTFE) particles in ethylene glycol was coated on one surface of a carbon paper, which was dried to produce a diffusion layer.

[0049]

#### (4) Production of electrode

The catalyst paste obtained in the step (2) was screen-printed on a primary layer of the diffusion layer, and after drying at 60°C for 10 minutes, vacuum drying was carried out at 120°C for 60 minutes to form a catalytic layer on the diffusion layer. Incidentally, the amount of the catalyst paste

coated was adjusted such that the amount of platinum on the electrode was  $0.5 \text{ mg/cm}^2$ . Thus, a pair of an oxygen electrode and a fuel electrode was obtained.

[0050]

5 (5) Production of membrane electrode assembly

A polymer electrolyte membrane obtained in the above step (1), which contained 15 weight % of an N-methylpyrrolidone organic solvent, was sandwiched by the oxygen electrode and the fuel electrode obtained in the above step (4), and hot-pressed at a temperature  $150^\circ\text{C}$  and a pressure of 2.5 MPa for 2 minutes, to produce a membrane electrode assembly. The whole  
10 membrane electrode assembly was introduced into a vacuum furnace to completely dry the polymer electrolyte membrane.

[0051]

EXAMPLE 6

15 A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane obtained in the step (5) of EXAMPLE 5, which contained 20 weight % of an N-methylpyrrolidone organic solvent, and hot-pressing at a temperature of  $120^\circ\text{C}$  and a pressure of 2.5 MPa for 2 minutes.

20 [0052]

EXAMPLE 7

A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane obtained in the step (5) of EXAMPLE 5, which contained 10 weight % of an  
25 N-methylpyrrolidone organic solvent, and carrying out a first hot-pressing at a temperature of  $80^\circ\text{C}$  and a pressure of 1.5 MPa for 2 minutes and then a second hot-pressing at a temperature of  $160^\circ\text{C}$  and a pressure of 2 MPa for 1 minute.

[0053]

EXAMPLE 8

A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane  
5 obtained in the step (5) of EXAMPLE 5, which contained 10 weight % of an N-methylpyrrolidone organic solvent, and carrying out a first hot-pressing at a temperature of 80°C and a pressure of 2.5 MPa for 2 minutes and then a second hot-pressing at a temperature of 160°C and a pressure of 2 MPa for 1 minute.

10 [0054]

EXAMPLE 9

A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane  
15 obtained in the step (5) of EXAMPLE 5, which contained 5 weight % of an N-methylpyrrolidone organic solvent, and hot-pressing at a temperature of 120°C and a pressure of 2.5 MPa for 2 minutes.

[0055]

COMPARATIVE EXAMPLE 3

20 A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane obtained in the step (5) of EXAMPLE 5, which contained 25 weight % of an N-methylpyrrolidone organic solvent, and hot-pressing at a temperature of 80°C and a pressure of 2.5 MPa for 2 minutes.

[0056]

25 COMPARATIVE EXAMPLE 4

A membrane electrode assembly was produced in the same manner as in EXAMPLE 5, except for using the polymer electrolyte membrane obtained in the step (5) of EXAMPLE 5, which contained 1 weight % of an

N-methylpyrrolidone organic solvent, and hot-pressing at a temperature of 180°C and a pressure of 2.5 MPa for 2 minutes.

[0057]

Evaluation of EXAMPLES 5-9 and COMPARATIVE EXAMPLES 3 and 4

5 (1) Measurement of Q value

Using the apparatus shown in Fig. 1, the Q value of each membrane electrode assembly in EXAMPLES 5-9 and COMPARATIVE EXAMPLES 3 and 4 was measured in a range from -0.1 V to +0.7 V. The measurement results are shown in Table 2.

10 [0058]

(2) Measurement of generated voltage

Using a single cell comprising each membrane electrode assembly in EXAMPLES 5-9 and COMPARATIVE EXAMPLES 3 and 4, electric power was generated with air supplied to the oxygen electrode and pure hydrogen  
15 supplied to the fuel electrode, to measure its cell voltage V at a current density  $i$  of 0.2A/cm<sup>2</sup>. The measurement conditions were pressure of 100 kPa, a utility percentage of 50%, a relative humidity of 50% and a temperature of 85°C for both of the oxygen electrode and the fuel electrode. The measurement results are shown in Table 2 and Fig. 3(b).

20 [0059]

(3) Measurement of percent defective

Using a single cell comprising each membrane electrode assembly in EXAMPLES 5-9 and COMPARATIVE EXAMPLES 3 and 4, a He gas at a pressure of 0.5 kPa was supplied to the cell from one side to measure the  
25 volume of a He gas passing through the cell to the other side per a unit time, thereby determining the amount of He leaked. By measuring 50 cells for each EXAMPLE and COMPARATIVE EXAMPLE, those in which the amount of He leaked was 0.1 ml/(cm<sup>2</sup> x minute) or more were counted as defective

products. The results are shown in Table 2 and Fig. 3(b).

[0060]

Table 2

Membrane electrode assembly using polymer electrolyte membrane  
made of sulfonated polysulfone

No.	Q value (C/cm <sup>2</sup> )	Remaining Solvent (wt. %)	Hot-Pressing		Percent Defective	Generated Voltage
			First	Second		
COM. EX. 3	0.05	25	80°C, 2.5 MPa, 2 min.	--	< 1%	0.60 V
EXAMPLE 5	0.09	15	150°C, 2.5 MPa, 2 min.	--	< 1%	0.70 V
EXAMPLE 6	0.11	20	120°C, 2.5 MPa, 2 min.	--	< 1%	0.72 V
EXAMPLE 7	0.13	10	80°C, 1.5 MPa, 2 min.	160°C, 2 MPa, 1 min.	< 1%	0.80 V
EXAMPLE 8	0.15	10	80°C, 2.5 MPa, 2 min.	160°C, 2 MPa, 1 min.	< 1%	0.81 V
EXAMPLE 9	0.18	5	120°C, 2.5 MPa, 2 min.	--	< 1%	0.80 V
COM. EX. 7	0.21	1	180°C, 2.5 MPa, 2 min.	--	14%	0.82 V

[0061]

As is clear from Table 2 and Fig. 3(b), when the membrane electrode assembly has a Q value of less than 0.09 C/cm<sup>2</sup>, voltage generated thereby is low, and when the Q value is more than 0.18 C/cm<sup>2</sup>, the percent defective is extremely high. Accordingly, in the membrane electrode assembly using sulfonated polysulfone as a sulfonated, non-fluorinated polymer, the polymer electrolyte membrane should have a Q value of 0.09-0.18 C/cm<sup>2</sup>.



[0062]

Although the polymer electrolyte membranes made of sulfonated polyetheretherketone and sulfonated polysulfone were used in the EXAMPLES mentioned above, the same effects as above were obtained as a result of experiment on polymer electrolyte membranes made of other polymers such as sulfonated polyethersulfone, sulfonated polyetherimide, sulfonated polyphenylene sulfide and sulfonated polyphenylene oxide.

[0063]

### Effect of the Invention

As described above in detail, according to the present invention, because the membrane electrode assembly comprises a high-softening-point polymer electrolyte membrane having a Q value in a desired range, it is possible to obtain the polymer electrolyte membrane having such a high heat resistance that it is not decomposed even by hot-pressing at high temperatures and a polymer electrolyte fuel cell comprising thereof.

### BRIEF DESCRIPTION OF THE DRAWINGS

**Fig. 1:** Fig. 1 is a schematic cross-sectional view showing an apparatus for measuring the Q value of the membrane electrode assembly of the present invention;

**Fig. 2:** Fig. 2 is a graph showing a discharge curve obtained as a result of measuring a current density in a predetermined voltage range, to determine the Q value of the membrane electrode assembly of the present invention; and

**Fig. 3:** Figs. 3(a) and 3(b) are graphs showing the relation between a Q value and a generated voltage and a percent defective in the membrane electrode assemblies of EXAMPLES COMPARATIVE EXAMPLES, that is;

Fig. 3(a) is a graph showing those in the membrane electrode assemblies of EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1 and 2, and

Fig. 3(b) is a graph showing those in the membrane electrode assemblies of EXAMPLES 5-9 and COMPARATIVE EXAMPLES 3 and 4.

**Explanations of the Symbols**

- 5    1 · · · Polymer Electrolyte Membrane,
- 2 · · · Catalytic Layer,
- 3 · · · Diffusion Layer,
- 4 · · · Primary Layer,
- 5 · · · Carbon Paper,
- 10   6 · · · Potentiostat,
- 7 · · · Control Electrode,
- 8 · · · Reference Electrode,
- 9 · · · Diluted Aqueous Sulfuric Acid Solution, and
- 10 · · · Electrode.

Fig. 1

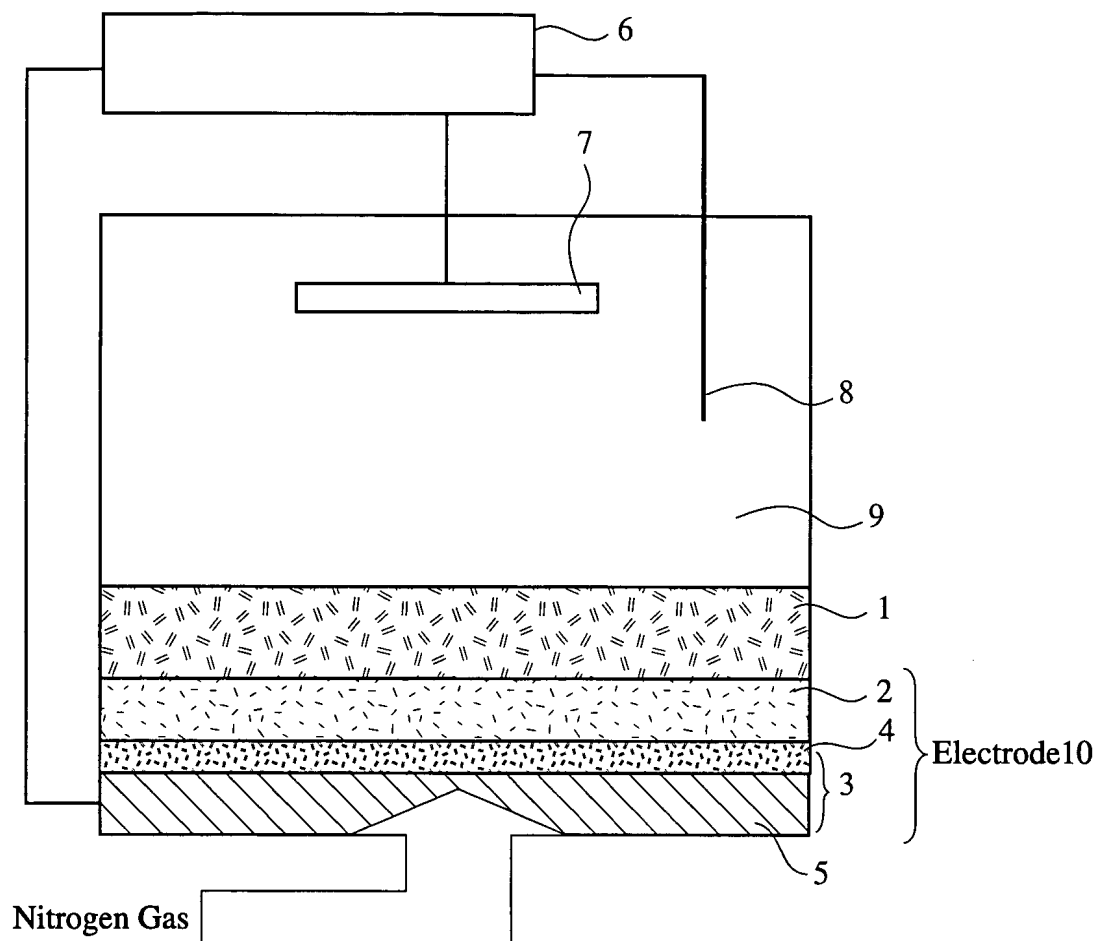
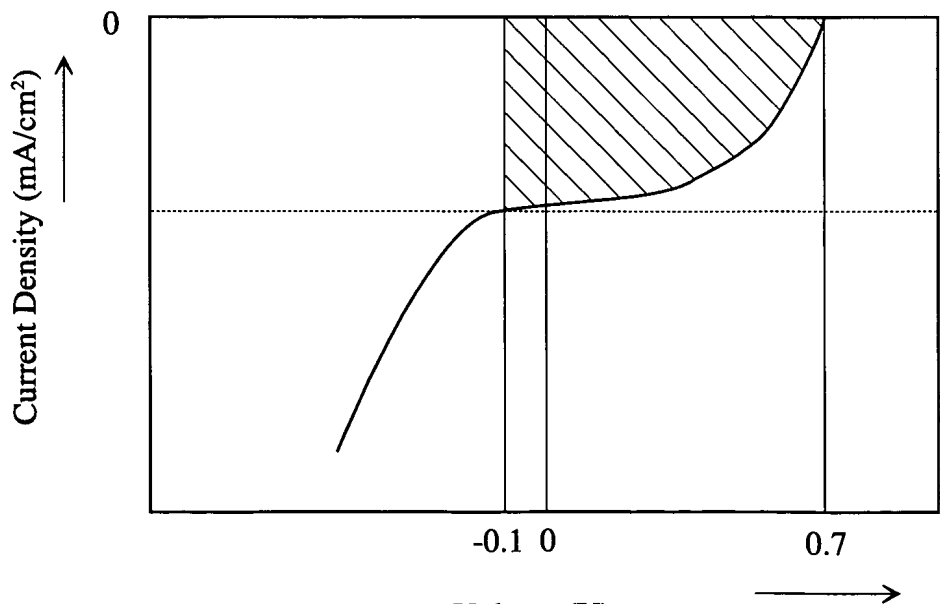
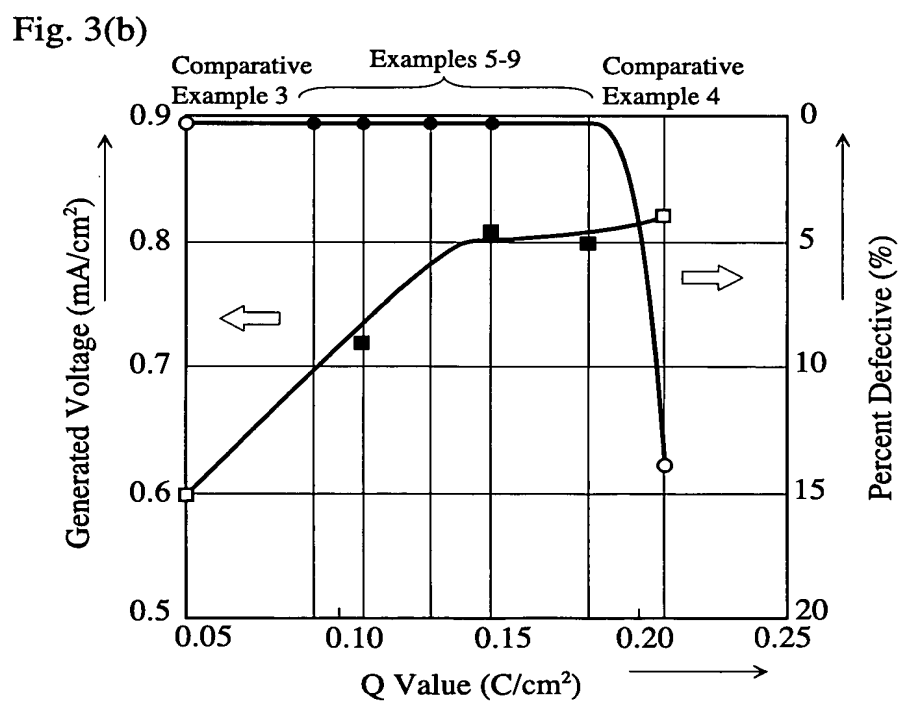
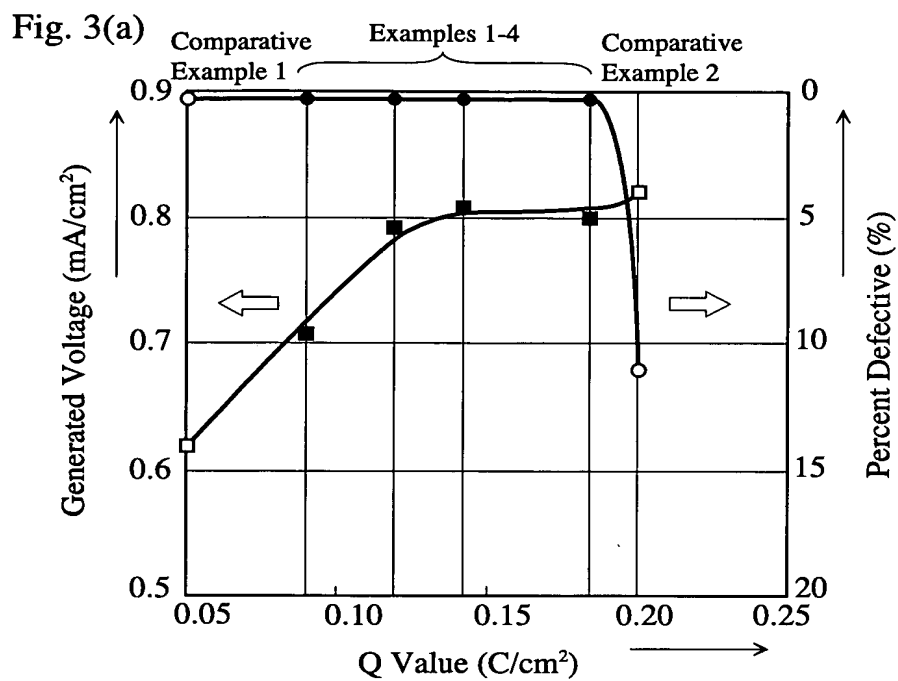


Fig. 2



# Fig. 3



**ABSTRACT**

**Problems to be solved by the invention:**

To provide a membrane electrode assembly comprising a polymer  
5 electrolyte membrane having not only a high power-generating  
performance but also such a high heat resistance that it is not decomposed  
by high-temperature hot-pressing.

**Solution:**

A membrane electrode assembly comprising a polymer  
10 electrolyte membrane, the polymer electrolyte membrane having a  
softening point of 120°C or more and a Q value of 0.09-0.18 C/cm<sup>2</sup>,  
wherein the membrane electrode assembly is produced by forming the  
polymer electrolyte membrane from a solution of the polymer electrolyte,  
hot-pressing the resultant polymer electrolyte membrane and a pair of  
15 electrodes arranged on both sides of the membrane, while the amount of the  
organic solvent remaining in the polymer electrolyte membrane is 3-20  
weight %, and followed by drying the polymer electrolyte membrane thus  
obtained.

20 **Selected Drawings:** None